

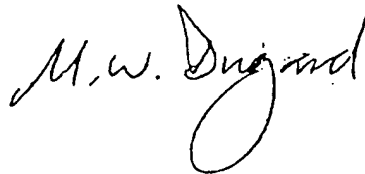
UK PATENTS ACT 1977 Section 77

IN THE MATTER of European  
Patent (UK) No. 0 448 000  
(Application No. 91104102.8)  
in the name of  
SOD-CHEMIE AG, et al

I, MELVYN WILLIAM DUGARD, M.I.T.I., A.I.L.,  
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Patent Attorneys, of 27, Farnival Street, London, EC4A 1PQ,  
do hereby certify that I am conversant with the English and  
German languages and am a competent translator thereof, and  
I verify that the attached translation corresponds to the  
original text of the German-language specification of  
European Patent (UK) No. 0 448 000 as granted.

Signed this 22nd day of August 1994

(Signature)



MELVYN WILLIAM DUGARD

# DESCRIPTION

The invention relates to a process for the preparation of lower olefins from methanol by conversion of a reaction mixture containing methanol vapour and/or dimethyl ether vapour and water vapour in a tubular reactor on an indirectly cooled catalyst based on crystalline aluminosilicates of the pentasil type with a Si/Al atomic ratio of at least 10.

A process of this type is known from US-A-4058576. Specifically, methanol is converted in this process in a first stage at least partially to dimethyl ether on an acidic catalyst, such as gamma-aluminium oxide, in an exothermic condensation reaction. Part of the reaction heat from the conversion of methanol to the lower olefins, which takes place in the second stage, can thus be reduced, since the heat produced in the exothermic reaction is less when using dimethyl ether as starting material than when using methanol.

The second stage involves a conversion over a crystalline zeolite of the type ZSM5. This zeolite is a crystalline aluminosilicate of the pentasil type with a Si/Al atomic ratio of at least 10.

The conversion in the second stage is carried out in a tubular reactor, producing lower olefins preferably with 3 or more carbon atoms ( $C_{3+}$  olefins). These lower olefins are then converted on the ZSM5-catalyst under specific operating conditions to hydrocarbons in the light benzine (gasoline) boiling range. The proportion of  $C_{3+}$  olefins and gasolines depends on the reaction conditions. The conversion is preferably carried out at increased pressure in order to better utilise the reactor volume.

US-A-4058576 offers no ideas on how to increase the propylene fraction in the resultant olefin mixture. Propylene represents an important raw material for the production of polypropylene, the propylene obtained from methanol being preferred over the propylene obtained from thermal cracking of hydrocarbons, since it is essentially free of sulphur compounds.

DE-A-36 04 636 describes a process by which methanol or dimethyl ether is converted to olefins on a dealuminised mordenite. The propylene content of the resultant hydrocarbon mixture is below 50 percent in spite of expensive recycling. It was apparently not recognised that the use of catalysts of the pentasil type and a reduction of the total pressure can increase the propylene fraction.

DE-C-32 28 269 describes a process for the conversion of alcohols and/or aliphatic ethers to unsaturated hydrocarbons with use of a catalyst which contains  $\text{ZnO}$  and/or  $\text{CdO}$  and whose zeolite is prepared with a sulfonium iodide. In spite of the use of a diluent ( $\text{N}_2$ ) at  $400^\circ\text{C}$  more undesirable  $\text{C}_9\text{-C}_{11}$ -hydrocarbons are formed than the desired propylene.

A similar process is known from US-A-4471150. This process employs a crystalline aluminosilicate modified with magnesium oxide, manganese oxide, or magnesium oxide/platinum oxide, for example a zeolite of ZSM-34 type in the H-form. The conversion of the methanol vapour and/or the dimethyl ether vapour can be carried out in a fixed bed or in a fluidised bed with diluents such as steam, more than 0.5 mole water per mole of organic reactants being preferably used. The total pressure is preferably between approximately 0.37 and 3.0 bar, atmospheric pressure being especially preferred.

The propylene content of the resultant olefin mixture is only between 21 and 29 percent by weight. It was apparently not recognised that the propylene fraction could have been increased by a reduction of the total pressure; the catalyst used, also had a relatively high alkali content even in the H-form (350 ppm Na, 1.47 percent K).

US-A-4025575 describes a process in which methanol and/or dimethyl ether along with a diluent, such as nitrogen, methane, or steam, are passed over catalysts based on crystalline aluminosilicates, in particular over zeolite catalysts of the HZSM5-type. The use of diluents causes a reduction of the methanol/dimethyl ether partial pressure to less than atmospheric pressure. Although it is mentioned that the total pressure in the reaction zone may be lower than atmospheric pressure, it is preferably between approximately 1 and 35 bar. The propylene content in the end product was only 33.75 percent by weight and the proportion of olefins having 5 or less carbon atoms ( $C_5$ -olefins) was only 64.10 percent by weight when water was used as the diluent at a total pressure of 1 bar and a methanol partial pressure of 0.50 bar (Example 19). The propylene fraction with 47.98 percent by weight and the  $C_5$ -olefin fraction with 86.77 percent by weight was highest when nitrogen was used (Example 7). The use of nitrogen as diluent has the disadvantage that the separation of the reaction product is more difficult, since the lower olefins can only be condensed at very low temperatures.

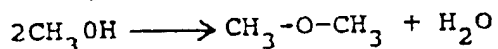
The separation of the lower olefins from the diluent is, of course, easier if water is used as diluent since it can be readily condensed from the reaction mixture.

It is therefore the object of this invention to improve the yield of lower olefins, in particular of propylene, in a process of the type defined above and simultaneously to facilitate the separation of the lower olefins from the diluent.

According to the invention this object is achieved in that to prepare an olefin mixture with at least 5% by weight of ethylene, at least 35% by weight of propylene and at most 30% by weight of butylene, in relation to the total hydrocarbons, the conversion is carried out

- a) at a total pressure of from 10 to 90 kPa,
- b) at a weight ratio between water and methanol or methanol equivalents of from 0.1 to 1.5,
- c) at a temperature of the reactor cooling medium of 280 to 570°C,
- d) on a proton-containing catalyst of the pentasil type with an alkali content of less than about 380 ppm (preferably less than 200 ppm, and particularly less than about 100 ppm), a ZnO content of less than about 0.1 percent by weight, a CdO content of less than about 0.1 percent by weight, a BET surface area of from 300 to 600 m<sup>2</sup>/g and a pore volume (determined by mercury porosimetry) of from 0.3 to 0.8 cm<sup>3</sup>/g.

As used in this invention, one "methanol equivalent" corresponds to 1/2 mol of dimethyl ether according to the equation



The water formed according to the equation is not added into the ratio under (b) above. The ratio between methanol vapour and dimethyl ether vapour can be varied within broad limits; in the extreme, 100 percent methanol or 100 percent dimethyl ether can be used. If a large fraction of dimethyl ether is used,

generated in a pre-stage from methanol on an acidic catalyst, the reaction heat from the olefin-generating reaction in the main stage is lower than that resulting from the use of a large methanol fraction. Using a series arrangement of a first stage and, optionally, an additional cooling stage, it is thus possible to control the strongly exothermic olefin-forming reaction in the main stage, permitting a reduction of the temperature increase in the catalyst of the main stage. Pure methanol can also be employed, however, in particular if the temperature of the reactor cooling medium is near the lower limit (feature c) or if the total pressure (feature a) is low or if the weight ratio between water and methanol (feature b) is high.

As a result of a combination of all the features, the process according to the invention provides a surprisingly high yield of propylene. It is also surprising that a reduction of the methanol partial pressure alone is not sufficient but that the total pressure must also be reduced. Under these conditions, the conversion apparently stops at the lower olefins i.e., no further reaction to higher olefins takes place. It is apparently also important that the catalyst contains a sufficient number of acid sites, i.e., it must have a very low alkali content.

Particularly favourable results are obtained, if the conversion is carried out at a total pressure of from 20 to 70, preferably from 30 to 60 kPa.

The conversion is preferably carried out at a weight ratio of water/methanol or methanol equivalents of from 0.2 to 1.0, in particular from 0.3 to 0.8.

The conversion is preferably carried out at a temperature of the reactor cooling medium of from 300 to 570, in particular from 350 to 500°C.

In a particularly preferred form of embodiment, the conversion is carried out in a salt bath tubular reactor, wherein the temperature in the catalyst should not exceed the temperature of the reactor cooling medium by more than  $60^{\circ}\text{C}$ . As a result of the exothermic reaction, a temperature peak (which should be kept as low as possible) develops along the catalysts bed, since the tendency of the initially formed ethylene towards further reaction increases with an increase of the temperature in the catalyst.

The structure of the catalyst used also plays an important role in increasing the yield of propylene. This structure consists preferably of primary crystallites with an average diameter of at least  $0.1\text{ }\mu\text{m}$  and at most  $0.9\text{ }\mu\text{m}$  which are partly combined to form agglomerates, wherein the primary crystallites and/or agglomerates are bonded together by finely divided aluminium oxide. The aluminium oxide is preferably obtainable by hydrolysis of alumino-organic compounds. The agglomerates of the catalyst have a large pore volume and relatively large pores as a result of this structure, permitting easy diffusion of the initially formed lower olefins and thereby suppressing further reactions on the surface of the catalyst. The catalysts used thus have high selectivity in addition to high activity.

Preferably, a catalyst is used with an average diameter of the primary crystallites between  $0.1$  and  $0.6\text{ }\mu\text{m}$ . If the average diameter is less than  $0.1\text{ }\mu\text{m}$ , the lifetime of the catalyst is reduced considerably; if the diameter exceeds  $0.9\text{ }\mu\text{m}$ , the initial activity is very low. The average diameter of the primary crystallites is defined as the arithmetic mean between the largest and smallest diameter of a single crystallite, averaged for a large number of crystallites. This definition is significant for

crystallites with an irregular crystal habitus, e.g., for rod-shaped crystallites. In the case of spherical or roughly spherical crystallites, the largest and smallest diameter coincide.

The primary crystallites in the catalysts to be used according to the invention can be combined into agglomerates of 5 to 500  $\mu\text{m}$  to the extent of at least 20 percent. These values again are average dimensions (arithmetic mean of the largest and the smallest dimension, averaged for many crystallites).

The composite bodies generally have dimensions of 20 to 1,000  $\mu\text{m}$ , in particular 50 to 800  $\mu\text{m}$ . The values again are average dimensions as defined above.

The catalyst structure of primary crystallites, agglomerates, and particles of binding agent also determines the BET surface area (300 to 600  $\text{m}^2/\text{g}$ ), the pore volume (0.3 to 0.8  $\text{cm}^3/\text{g}$ ), and the pore diameter, i.e., at least 20 percent of the pores have preferably a diameter of 14 to 30 nm.

The BET surface area, the pore volume, and the pore diameter represent the optimum choice for catalysts with high activity, selectivity and a durability.

The amount of finely divided aluminium oxide binding agent is preferably 10 to 40 percent by weight, relative to the weight of the end product.

The finely divided aluminium oxide binding agent is preferably present in the reaction mixture as peptised aluminium oxide hydrate, at least 95 percent of whose particles (relative to the average diameter) are  $\leq 55 \mu\text{m}$ . The finely divided aluminium oxide binding agent can preferably be obtained by hydrolysis of aluminium trialkyls or aluminium alcoholates.

The catalyst to be used according to the invention can preferably be obtained in the following



way:

- (a) an alkaline aluminosilicate gel is prepared in per se known manner in an aqueous reaction mixture, containing a source of silicon, a source of aluminium, a source of alkali and a template at elevated temperature and, if desired, at elevated pressure and converted to a crystalline aluminosilicate, the reaction being terminated when the resultant primary crystallites reach an average diameter of at least  $0.1\ \mu\text{m}$  and at most  $0.9\ \mu\text{m}$ , preferably  $0.1$  to  $0.6\ \mu\text{m}$ ;
- (b) the primary crystallites are separated from the aqueous reaction medium as preagglomerates, dried and subjected to an intermediate calcination;
- (c) in order to exchange the alkali ions, the product of step (b) is reacted in an aqueous medium with a proton-containing substance or with a substance which supplies protons upon heating until the alkali content is below 380 ppm, preferably below 200 ppm, and in particular below 100 ppm, separated, dried and again subjected to an intermediate calcination, whereupon an agglomerate fraction of approximately 5 to  $500\ \mu\text{m}$  is separated;
- (d) the agglomerate fraction of step (c) is mixed with the finely distributed aluminium oxide hydrate;
- (e) the product of step (d) is subjected to a final calcination.

The significance of the individual steps, according to which the catalyst used according to the invention can be obtained, is explained in more detail below:

Step (a) involves firstly the preparation of an aqueous reaction mixture, containing a source of silicon (for example colloidal silicic acid or an alkali silicate), a source of aluminium (for example aluminium hydroxide or sodium aluminate), a source of alkali (for example an alkali hydroxide, in which case the alkali source may also be part of the silicon source, if alkali silicates are used, or part of the aluminium source, if alkali aluminates are used), and a template. The weight ratios between the source of silicon and the source of aluminium are chosen in such a way that crystalline aluminosilicates with a Si/Al atomic ratio of at least 10, preferably approximately 20 to 500:1 are obtained. An alkaline aluminosilicate gel is prepared from the reaction mixture at elevated temperature and possibly elevated pressure in per se known manner. Temperatures as low as 90°C can be used, but the reaction times are relatively long in this case (approximately 1 week). Preferred temperatures are from 90 to 190°C, especially from 90 to 150°C; if temperatures of more than 100°C (under standard conditions) are used, an overpressure is automatically established as a function of the temperature.

The aluminosilicate gel is converted to a crystalline aluminosilicate in the course of the reaction. If the temperature of the reaction mixture exceeds 190°C, the growth of the aluminosilicate primary crystallites becomes too fast and primary crystallites with a diameter of more than 0.9  $\mu\text{m}$  are obtained, while aluminosilicate gel is still present in the reaction mixture.

Tetraalkylammonium compounds, preferably tetrapropylammonium hydroxide (TPAOH) or tetrapropylammonium bromide (TPABr), are used as templates. Mixtures of ammonia or an organic amine and another organic compound from the group of alcohols, preferably butanol, can also be used as templates.

The aqueous reaction mixture of step (a) has a pH value of preferably 10 to 13. At a pH value below 10, the conversion of the aluminosilicate gel to the crystalline aluminosilicate is relatively slow. At pH values above 13, the aluminosilicate crystals can dissolve again in certain cases. This can generally be tolerated, however, since usually only the smallest primary crystallites with a diameter of less than 0.1  $\mu\text{m}$  are dissolved.

The formation of crystalline aluminosilicate primary crystallites can be controlled by suitable selection of the source of silicon, the source of aluminium, the source of alkali, and the template as well as by suitable selection of the temperature, the pH value, and the stirring speed. It is important to terminate the reaction when the resultant primary crystallites have an average diameter of at least 0.1  $\mu\text{m}$  and at most 0.9  $\mu\text{m}$ .

Several test batches were run for this purpose. The optimum parameters, which produce the required range of sizes of the primary crystallites, can be determined after only a few tests. One indication for the end of the reaction is the fact that the pH-value of the reaction mixture increases sharply.

According to the invention, it is not necessary to prepare a new reaction mixture in every case. In order to prepare the aluminosilicate gel, the source of silicon, the source of alkali, the source of aluminium, the template, and the water from the mother

liquors of previous syntheses can be used, complemented by the amounts of said compounds which are necessary for the synthesis of the aluminosilicate gel.

The formation of the aluminosilicate primary crystallites of step (a) is preferably carried out at a pH value between 10 and 13 with stirring of the reaction mixture. The size distribution of the primary crystallites is thus homogenised. The stirring speed should preferably not exceed 900 RPM, however. Higher stirring speeds produce a larger fraction of smaller primary crystallites, requiring a longer reaction time to ensure that the average diameter of all primary crystallites is at least 0.1  $\mu\text{m}$ .

Step (b) involves the separation of the primary crystallites from the aqueous reaction medium as preagglomerates, i.e., not as individual crystallites. This is preferably achieved in such a way that a flocculating agent is added to the aqueous reaction medium. The flocculating agent is generally a cationic organic macromolecular compound, preferably a copolymer of acrylamide and a cationic acrylic acid derivative.

The flocculating agent not only facilitates the separation of the primary crystallites from the reaction medium (improved filterability), but it also causes the combination of the primary crystallites to preagglomerates which are already largely similar to the agglomerates produced in the following step with regard to size, structure, and aggregation of primary crystallites. The preagglomerates are dried and subjected to an intermediate calcination, which is initially carried out in an inert atmosphere at approximately 200 to 350°C, in particular at

approximately 250°C, during which a part of the template is desorbed.

The intermediate calcination can then be completed in an oxidising atmosphere at approximately 500 to 600°C, through which any remaining residual amount of template is burned off.

The preagglomerates are treated for approximately 1 to 20 hours in the inert atmosphere and for approximately 1 to 30 hours in the oxidising atmosphere as part of the intermediate calcination.

Step (c) involves the reaction of the product from step (b) in an aqueous medium with a proton-containing substance or with a substance which supplies protons upon heating for the purpose of exchanging the alkali ions. The ion exchange can, for example, be carried out with a dilute mineral acid (e.g. hydrochloric or sulphuric acid) or with an organic acid (e.g. acetic acid). The ion exchange is preferably carried out for at least one hour with stirring at temperatures between 25 and 100°C, whereby at least one part of the alkali ions in the preagglomerates of the primary crystallites are exchanged by hydrogen ions. The ion exchange can be repeated under the same conditions, if necessary.

Following the exchange of the alkali ions in an aqueous medium, the proton-containing product (H-zeolites) is separated (for example by filtration), dried and again subjected to an intermediate calcination. This intermediate calcination is carried out at temperatures between 400 and 800°C, preferably at approximately 600°C over a period of 5 to 20 hours.

Instead of using dilute acid, an ammonium salt solution can also be used under comparable conditions for the ion exchange. The alkali ions are replaced by ammonium ions in this case. If the resultant product

is subjected to intermediate calcination, ammonia is removed and a proton-containing product is obtained.

The product obtained after intermediate calcination contains agglomerates of  $\geq 500 \mu\text{m}$  and dust fractions of  $\leq 5 \mu\text{m}$ . Thus, an agglomerate fraction from approximately 5 to  $500 \mu\text{m}$  is separated.

This agglomerate fraction is mixed with finely divided aluminium oxide hydrate in step (d), the latter containing at least 95 percent  $\leq 55 \mu\text{m}$  and at least 30 percent  $\geq 35 \mu\text{m}$ . These values, averaged over many crystallites, are each related to the mean diameter, which is defined in the same way as the mean diameter of the primary crystallites. The aluminium oxide typically shows the following particle size distribution:

99 percent  $\leq 90 \mu\text{m}$

95 percent  $\leq 45 \mu\text{m}$

55 percent  $\leq 25 \mu\text{m}$ .

The aluminium oxide hydrate is largely responsible for adjusting the pore volume of the catalyst according to the invention. The amount of finely divided aluminium oxide hydrate binding agent is preferably approximately 10 to 70 percent by weight, relative to the total weight of the product of step (d). The finely divided aluminium oxide hydrate binding agent is preferably a peptisable aluminium oxide which is particularly low in Na and Fe.

The peptisation is preferably carried out with a dilute, weak acid.

The product of step (d) is subjected to a final calcination. This calcination can be carried out at temperatures of approximately 400 to  $800^{\circ}\text{C}$ , preferably at approximately  $540^{\circ}\text{C}$ , over a period of 5 to 20 hours.

The catalyst, which is preferably used according to the invention, is described in detail in EP-A-369364.

The process according to the invention is described with reference to the drawing.

Methanol is supplied via line 1, heated in heat exchanger 2 to temperatures of approximately 250 to 350°C and evaporated thereby. The methanol vapour is fed to a pre-reactor via line 3, which contains a bed 5 of granular dehydration catalyst. The catalyst can be aluminium oxide as described in US-PS4058576, for example. A part of the methanol is converted to dimethyl ether and water in the pre-reactor 4 and the resultant mixture is removed via line 7.

The reaction in pre-reactor 4 reduces the heat generation in the downstream tubular reactor 8. A metered amount of steam is added via line 9 to the mixture of line 7; the steam originates from the heat exchanger. Cooling water for the generation of the steam is supplied to the heat exchanger 10 via line 11. The tubular reactor 8 is charged via line 12 with a mixture of methanol, dimethyl ether and steam, the temperature of which is between approximately 250 and 450°C. The mixture of line 12 has a water/methanol equivalent weight ratio of 0.1 to 1.5, preferably 0.2 to 1.0, and particularly of at most 0.8 (1 mol DME = 2 mol methanol equivalent). The catalyst is arranged in numerous tubes in the tubular reactor 8; the tubes commonly have lengths of 1 to 5 m and an internal diameter of 20 to 50 mm.

With respect to the conversion of methanol and DME to the desired lower olefins, in particular ethylene and propylene, it is recommended to use thorough cooling of the catalyst and a subatmospheric total pressure in the catalyst region of 10 to 90 kPa, preferably 20 to 70 kPa, and in particular 30 to 60

kPa. The indirect cooling of the catalyst, which is arranged in the tubes, is carried out by a salt bath. The salt bath is supplied to reactor 8 via line 15, leaves the reactor via line 16, releases heat in a heat exchanger 17 and returns to reactor 8. The heat exchanger 17 is supplied with feed water via line 18 and high-pressure steam is removed via line 19.

The conversion on the catalyst of the tubular reactor 8 takes place at temperatures between 280 and 570°C, preferably at a temperature of at least 300°C, and in particular between 350 and 500°C. If a fused salt is used as cooling medium, it is possible to maintain a temperature in the catalyst, which does not exceed the temperature of the salt bath by more than 60°C. Damage to the catalyst through excessive peak temperatures is avoided thereby; surprisingly, it is also found that the yield of propylene is increased and that the production of butylene is reduced as desired.

The product mixture leaves the tubular reactor 8 through line 20, is subjected to initial cooling in heat exchanger 10, flows through line 21 to heat exchanger 2, whereupon the product partially condenses. The product flows via line 22 to a separation container 23, from which the vaporous, lower olefins are removed by suction through vacuum pump 24 and become available as product mixture in line 25. The condensate collecting in the container separates into water and benzene hydrocarbons; the water is removed through line 26 and the benzene hydrocarbons are removed through line 27.

The invention is illustrated by the following examples.



### Preparation Example

According to this example aluminosilicate zeolites with a primary crystallite size of  $<1\mu\text{m}$  were prepared. Specifically, the procedure was as follows:

A reaction mixture was prepared by intimately mixing two solutions at room temperature in a 1,000 litre agitated pressure vessel. The two solutions were designated solution A and solution B. Solution A was prepared by dissolving 95.7 kg TPABr in 600 litres of deionised water. 215.8 kg of a commercially available silicic acid were added to this solution. Solution B was prepared by dissolving 33.1 kg NaOH and then 2 kg  $\text{NaAlO}_2$  in 50 litres of deionised water. Solution B, still warm, was then added to solution A. Another 62 litres of deionized water were added. The autoclave was then closed and heated to the reaction temperature with stirring at approximately 600 to 800 RPM. The reaction was completed after approximately 50 hours, as indicated by the sudden shift in pH value (from 11.6 to 12.2). Following cooling, the pressure container was opened and the product was removed from the reaction vessel and filtered. The filter cake was suspended, treated with a 0.4 percent by weight aqueous suspension of a commercially available flocculating agent, and decanted after stirring and settling of the preagglomerates of the solid. This wash process was repeated until the wash water had a pH value of 7 to 8 and a Br-concentration of less than 1 ppm. The suspension, in which preagglomerates of primary crystallites were evident, apparently being held together by the flocculating agent, was filtered. The freely filterable filter cake was then dried at  $120^\circ\text{C}$  for 12 hours and calcined at  $540^\circ\text{C}$  for 24 hours. The size of the primary crystallites is listed in Table I. The conditions required to achieve

the desired crystallite sizes had been determined earlier in serial experiments.

The dried filter cake was comminuted prior to calcination with a commercial granulator to a particle size of less than 2 mm.

The granulate was heated to 350°C under nitrogen (1,000 Nl/h), using a rate of heating of 1°C/min, and then calcined at 350°C for 15 hours under nitrogen (1,000 Nl/h). The temperature was then increased to 540°C at a heating rate of 1°C/min and the granulate was calcined for 24 hours at this temperature in air in order to burn off the remaining TPA. The calcined Na-zeolite was analysed, yielding the values shown in Table I.

The calcined Na-zeolite was suspended in the 5-fold amount of a 1-molar aqueous solution of HCl and heated to 80°C. The suspension was stirred at this temperature for 1 hour. A 0.4 percent by weight suspension of the flocculating agent was then added and the supernatant acid was decanted off after settling of the solid matter. This process was repeated once.

The solid matter was suspended with stirring in 10 wash cycles in approximately 300 litres of deionised water each and mixed with a 0.4 percent by weight suspension of the flocculating agent. Following settling of the zeolite, the supernatant solution was decanted off. When the  $\text{Cl}^-$  concentration in the wash water was < 5 ppm, the suspension was filtered and dried for 15 hours at 120°C. The sodium content was approximately 340 ppm, the potassium content was below 22 ppm.

The dried H-zeolite was comminuted to < 2 mm with a commercially available granulator, heated to 540°C under air at a rate of 1°C/min, and calcined at this

temperature under air for 10 hours. The specifications of this calcined H-zeolite are listed in Table I.

5,000 g of the calcined H-zeolite were ground with the aid of a laboratory mill to a particle size  $< 500 \mu\text{m}$  and mixed in the dry state for 15 minutes in a double-Z-kneader with 1,470 g of a commercial, peptisable aluminium oxide hydrate with the following particle size distribution:

99 percent by weight  $\leq 90 \mu\text{m}$

95 percent by weight  $\leq 45 \mu\text{m}$

55 percent by weight  $\leq 25 \mu\text{m}$

A 17 percent by weight aqueous solution of nitric acid (for peptisation of the aluminium oxide hydrate) and steatite oil were slowly added to this mixture.

This mixture was kneaded for approximately 30 minutes until plasticized and then extruded with a commercial extruder to yield mouldings of approximately 3 mm diameter and 6 mm length. The final calcination was carried out for 5 hours at  $600^{\circ}\text{C}$ .

The analytical data and the chemical and physical characteristics of the product are set out in Table I.

TABLE I

Molar ratios of the starting materials

$\text{SiO}_2$	100
$\text{NaAlO}_2$	0.67
$\text{NaOH}$	23
$\text{TPABr}$	10
$\text{H}_2\text{O}$	1,100

Crystallisation data

temperature ( $^{\circ}\text{C}$ )	130
time (h)	50
crystallinity (%)	100
primary crystallite size ( $\mu\text{m}$ )	0.3

Si and Al contents of the Na-zeolite

Si (% by weight)	45.0
Al (% by weight)	0.42
Si/Al (atomic ratio)	103

Physical and chemical characteristics of the catalyst

BET surface area ( $\text{m}^2/\text{g}$ )	342
pore volume ( $\text{cm}^3/\text{g}$ )	0.33
pores $\geq 80$ nm (%)	25.1
pores 14-80 nm (%)	68.1
Na-content (ppm)	approx. 340

APPLICATION EXAMPLE 1

Steam was added via line 9 to a mixture of methanol and dimethyl ether vapour obtained from pre-reactor 4. The temperature of the mixture before entering the tubular reactor 8 was  $400^{\circ}\text{C}$ . The weight ratio between steam and methanol vapour (line 3) was 1.0; the space velocity was 0.5 kg total methanol used per kg catalyst and per hour. The product mixture leaving the tubular reactor 8 was first cooled in heat exchanger 10 and then partially condensed in heat exchanger 2. The lower olefins were removed via line 25. The condensate trapped in container 23 separated into water and benzene hydrocarbons, the water being removed via line 26 and the benzene hydrocarbons being removed via line 27.

The tubular reactor 8 was operated as a single tube, which was filled with 1.2 litres of the catalyst as described in the example of preparation. The temperature in the salt bath was 439°C; the salt consisted of a mixture of 44 mol-%  $\text{KNO}_3$ , 7 mol-%  $\text{NaNO}_2$  and 49 mol-%  $\text{NaNO}_3$ .

The catalyst in the salt bath reactor was kept at a subatmospheric total pressure of 50 kPa by continuously removing the resultant reaction products via vacuum pump 24.

The results are set out in Table II.

#### APPLICATION EXAMPLE 2

The process of Application Example 1 was repeated with the difference that the temperature of the salt bath was adjusted to 439°C, the space velocity was 1.0 kg methanol per kg catalyst and hour, and the weight ratio of the steam fed through line 9 to the methanol vapour of line 3 was 0.5. These results are set out in Table II.

#### APPLICATION EXAMPLE 3

The process of Application Example 2 was repeated with the difference that the total pressure was reduced to 40 kPa.

The results are set out in Table II.

TABLE II

<u>Application Example</u>	<u>1</u>	<u>2</u>	<u>3</u>
pressure (kPa)	50	50	40
salt bath temperature (°C)	428	439	439
maximum catalyst temperature (°C)	458	475	468
space velocity (kg/kg x h)	0.5	1.0	1.0
steam/methanol vapour (kg/kg)	1.0	0.5	0.5
methanol conversion (%)	99.9	99.7	99.3

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hydrocarbon distribution in the product


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<u>paraffins</u> ( $C_1-C_4$ ) (% by weight)	5.58	5.10	4.75
<u>olefins</u> $C_2$ (% by weight)	7.27	6.82	6.00
$C_3$ (% by weight)	42.14	44.37	47.63
$C_4$ (% by weight)	<u>25.66</u>	<u>23.95</u>	<u>22.49</u>
total (% by weight)	75.07	75.14	76.12
<u>gasoline</u> $C_5+$ (% by weight)	19.35	19.76	19.13

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APPLICATION EXAMPLES 4 to 8 (COMPARISON)

The process of Application Example 1 was repeated, the difference being that the parameters were varied as indicated in Table III. In particular, the total pressure of the reactants was 100 kPa (1.0 bar), the space velocity was always 0.5 kg/kg x h and the ratio of steam (line 9) to methanol vapour (line 3) was 1.0 kg/kg. Although the partial pressure of methanol was only 36 kPa because of the steam/methanol ratio of 1.0 kg/kg, this is not sufficient to achieve the desired high yield of propylene. It is, in fact, also necessary for the total pressure of the reactants to be below atmospheric pressure.

TABLE III

Application Example (comparison)	4	5	6	7	8
salt bath temperature ( $^{\circ}\text{C}$ )	397	416	428	435	442
maximum cat. temp. ( $^{\circ}\text{C}$ )	456	473	484	491	496
methanol conversion (%)	99.9	99.9	99.9	99.9	99.9

hydrocarbon distribution in the product

<u>paraffins</u> ( $\text{C}_1\text{-C}_4$ ) (% by weight)	13.02	11.51	10.68	10.08	9.92
<u>olefins</u> $\text{C}_2$ (% by weight)	6.46	8.09	8.84	10.21	10.46
$\text{C}_3$ (% by weight)	20.87	25.77	28.23	29.96	31.21
$\text{C}_4$ (% by weight)	<u>18.48</u>	<u>20.08</u>	<u>20.77</u>	<u>20.62</u>	<u>21.17</u>
total (% by weight)	45.80	53.94	57.84	60.79	62.84
<u>gasoline</u> $\text{C}_5+$ (% by weight)	41.18	34.55	31.48	29.13	27.24

CLAIMS

1. A process for the preparation of lower olefins from methanol by conversion of a reaction mixture containing methanol vapour and/or dimethyl ether vapour and water vapour in a tubular reactor on an indirectly cooled catalyst based on crystalline aluminosilicates of the pentasil type with a Si/Al atomic ratio of at least 10, characterised in that to prepare an olefin mixture with at least 5 % by weight of ethylene, at least 35 % by weight of propylene and at most 30 % by weight of butylene, in relation to the total hydrocarbons, the conversion is carried out

- (a) at a total pressure of from 10 to 90 kPa,
- (b) at a weight ratio between water and methanol and/or methanol equivalents of from 0.1 to 1.5,
- (c) at a temperature of the reactor cooling medium of from 280 to 570°C,
- (d) on a proton-containing catalyst of the pentasil-type with an alkali content of less than 380 ppm, a ZnO content of less than 0.1 % by weight, a CdO content of less than 0.1 % by weight, a BET surface area of from 300 to 600 m<sup>2</sup>/g and a pore volume (determined by mercury porosimetry) of from 0.3 to 0.8 cm<sup>3</sup>/g.

2. A process according to Claim 1, characterised in that the conversion is carried out at a total pressure of from 20 to 70, preferably from 30 to 60 kPa.

3. A process according to Claim 1 or 2, characterised



in that the conversion is carried out at a weight ratio of water/methanol or methanol equivalents of from 0.2 to 1.0, preferably from 0.3 to 0.8.

4. A process according to any one of Claims 1 to 3, characterised in that the conversion is carried out at a temperature of the reactor cooling medium of from 300 to 570, preferably from 350 to 500°C.

5. A process according to any one of Claims 1 to 4, characterised in that the conversion is carried out in a salt bath tubular reactor, wherein the temperature in the catalyst does not exceed the temperature of the reactor cooling medium by more than 60°C.

6. A process according to any one of Claims 1 to 5, characterised in that the conversion is carried out on a catalyst which is composed of primary crystallites with an average diameter of at least 0.1  $\mu\text{m}$  and at most 0.9  $\mu\text{m}$ , which are partly combined to form agglomerates, wherein the primary crystallites and/or agglomerates are bonded together by finely divided aluminium oxide.

7. A process according to any one of Claims 1 to 6, characterised in that a catalyst is used in which the average diameter of the primary crystallites is in the region of from 0.1 to 0.6  $\mu\text{m}$ .

8. A process according to any one of Claims 1 to 7, characterised in that a catalyst is used whose primary crystallites are combined up to at least 20 % to form agglomerates of from 5 to 500  $\mu\text{m}$ .

9. A process according to any one of Claims 1 to 8, characterised in that a catalyst is used, of which at least 20 % of the pores have a diameter of from 14 to 80 nm.

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